



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : B29C 67/24		A1	(11) International Publication Number: WO 92/1832 (43) International Publication Date: 29 October 1992 (29.10.92)
<p>(21) International Application Number: PCT/US92/03293</p> <p>(22) International Filing Date: 22 April 1992 (22.04.92)</p> <p>(30) Priority data: 690,134 23 April 1991 (23.04.91) US</p> <p>(60) Parent Application or Grant (63) Related by Continuation US 690,134 (CIP) Filed on 23 April 1991 (23.04.91)</p> <p>(71) Applicant (for all designated States except US): LANXIDE TECHNOLOGY COMPANY, LP [US/US]; 1300 Marrows Road, P.O. Box 6077, Newark, DE 19714-6077 (US).</p>			
<p>(72) Inventors; and (75) Inventors/Applicants (for US only) : LOOBY, Christopher Mark [US/US]; 3 Hunting Court, Newark, DE 19711 (US). WEINSTEIN, Jerry, Glenn [US/US]; 321 Laure Avenue, Newark, DE 19711 (US). McELWEE, David Marc [US/US]; 8 Westfield Drive, Newark, DE 19711 (US). GODLBERG, Perry, Brian [US/US]; 20 Mahogany Drive, North East, MD 21901 (US).</p> <p>(74) Agents: MORTENSON, Mark, G. et al.; Lanxide Corporation, 1300 Marrows Road, P.O. Box 6077, Newark, DE 19714-6077 (US).</p> <p>(81) Designated States: AT (European patent), BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, LU (European patent), MC (European patent), NL (European patent), SE (European patent), US.</p> <p>Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</p>			
<p>(54) Title: POLYMER MATRIX COMPOSITE BODIES AND METHODS FOR MAKING THE SAME</p> <p>(57) Abstract</p> <p>This invention relates generally to a novel process for making self-supporting polymer matrix composite bodies, and the novel products produced thereby. More specifically, an appropriate filler material is caused to be placed within a particular polymer material, whereby the polymer material functions as a matrix and the filler material synergistically interacts with the polymer to form a novel composite body. By combining specific polymer matrix materials with specific filler or reinforcing materials, very desirable wear parts can be fabricated.</p>			

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	ES	Spain	MC	Madagascar
AU	Australia	FI	Finland	ML	Mali
BB	Barbados	FR	France	MN	Mongolia
BE	Belgium	CA	Gabon	MR	Mauritania
BF	Burkina Faso	GB	United Kingdom	MW	Malawi
BG	Bulgaria	GN	Guinea	NL	Netherlands
BJ	Benin	GR	Greece	NO	Norway
BR	Brazil	HU	Hungary	PL	Poland
CA	Canada	IT	Italy	RO	Romania
CF	Central African Republic	JP	Japan	RU	Russian Federation
CG	Congo	KP	Democratic People's Republic of Korea	SD	Sudan
CH	Switzerland	KR	Republic of Korea	SE	Sweden
CI	Côte d'Ivoire	LI	Liechtenstein	SN	Senegal
CM	Cameroon	LK	Sri Lanka	SU	Soviet Union
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
DE	Germany	MC	Monaco	TG	Togo
DK	Denmark			US	United States of America

- 1 -

DESCRIPTION

5

POLYMER MATRIX COMPOSITE BODIES AND METHODS FOR MAKING THE SAME

Technical Field

This invention relates generally to a novel process for making self-supporting polymer matrix composite bodies, and the novel products produced thereby. More specifically, an appropriate filler material is caused to be placed within a particular polymer material, whereby the polymer material functions as a matrix and the filler material synergistically interacts with the polymer to form a novel composite body.

10 By combining specific polymer matrix materials with specific filler or reinforcing materials, very desirable wear parts can be fabricated.

15

Background Art

The premature wear of surfaces of components for use in various structures has long been a problem facing product manufacturers in many diverse industrial fields. For example, wherever one component is contacted with another component in a sliding, abrading or impacting manner, at least one of the two components has a tendency to wear or abrade away. Such contact may occur between two solid parts, or a solid part that is placed into contact with a solid suspended within a liquid, etc. This type of wear or abrasion of components leads to the inability to continue to permit contact between the components due to material loss from at least one of the components. Material loss can result in, for example, mechanical failure of a component (e.g., fracture), impermissible tolerances between components previously tightly fitting together, etc.

20

25

30

Accordingly, the art is replete with attempts to manufacture new and improved components which are more resistive to wear or abrasion than those previously known. Attempts have been made to manufacture wear resistant parts for many different applications including high temperature wear resistance, low temperature wear resistance, dry erosion wear resistance, wet erosion wear resistance, etc. A major motivating factor in the manufacture of materials having desirable wear properties includes, among other considerations, cost and ease of manufacture of materials,

35

- 2 -

ability to shape materials to net or near-net shapes and large sizes and wear performance of materials.

Some exemplary materials which have been utilized for wear parts include certain ceramic materials such as sintered silicon carbide and sintered alumina, certain metals such as Stellite, Ni-Hard, Ni-Resist, etc., and certain polymers or resins such as polybutylene terephthalate (PBT), Polyetherimide and polyurethanes. However, the search for an economically producible and highly wear resistant part still continues.

The art also includes various attempts to combine certain filler materials in a polymer matrix to attain differing results. A first such attempt to combine a filler material with a polymer is disclosed in U.S. Patent No. 3,585,100, to W. D. Greenlees, which issued on June 15, 1971. This Patent discloses that a hard mar-resistant surface can be manufactured by mixing a crushed quartz filler material with a resin. Specifically, it is disclosed that in a preferred embodiment, 80% by weight crushed quartz, when mixed with 20% by weight of a resin material, can result in a panel structure having a hard mar-resistant surface. The panel structure is made by mixing the quartz and resin together. The resultant mixture is poured into a rubber mold, said mold being vibrated to cause the quartz to settle to the bottom portion of the mold, thus producing quartz-rich and resin-rich layers. A honeycomb structure is thereafter pressed into the resin-rich layer and further processing occurs to result in a hard mar-resistant surface on a lightweight panel structure.

U.S. Patent No. 2,751,775, to J. A. Sergovic, which issued on June 26, 1956, discloses a method for producing a cast resin surface containing particles (e.g., sand particles) as a coating on a substrate material (e.g., masonry building blocks). Specifically, it is disclosed that a sand filler material is mixed with resin, and the resultant slurry is poured into a vibrating mold. The sand is typically present in an amount of at least about 50% by weight. The vibrating mold causes the slurry to level out and removes entrapped air from the slurry. After the slurry has levelled out and entrapped air has been removed, a substrate material (e.g., a masonry block) is lowered into the mold and the resin is permitted to cure on the substrate as a surface, thus providing the substrate with an attractive and protective coating.

- 3 -

A further attempt to form an abrasion resistant material is disclosed in U.S. Patent No. 3,888,714, to J. T. Fiser, which issued on June 10, 1975. This patent discloses a method for providing an abrasion resistant surface on the inner layer of a tubular article (e.g., pipes and conduits). The disclosed reinforcing pipes and conduits can be used, for example, to transport rock or metal ores in dry or slurry form. Specifically, a fibrous material is first wrapped around a mandrel, said fibrous material thereafter being impregnated with an uncured resin. Abrasion resistant particles are then sprinkled onto the fibrous material/resin combination while the mandrel is rotated. The procedure is repeated until a uniform and relatively thick layer of abrasion resistant particles is applied. A second fibrous material is wrapped around the abrasion resistant layer and impregnated with a resin to complete the liner. Finally, fibrous filaments impregnated with a thermo-setting resin are applied about the liner and the composite is cured, thus forming an abrasion and corrosion resistant article. The patent further discloses a preference for cheesecloth as the fibrous material, ceramic particles (e.g., alumina) as the filler material and an epoxy-type resin having a viscosity of from, for example, 2000 to 20,000 centipoise for securing the abrasion resistant ceramic particles to the fibrous material.

Additionally, it is further disclosed that it is desirable to provide the ceramic filler material with at least a partial surface coating of metal adapted to adhere to the resin material.

While the art discloses a number of different techniques for the manufacture of wear resistant articles, as well as disclosing a number of different articles produced thereby, the search still continues for an uncomplicated, economical and reliable method for making wear resistant articles having desirable physical properties. The present invention satisfies this long felt need by providing a simple process for the manufacture of net or near-net shape wear parts by combining materials and processing steps in a novel manner.

Description of Commonly Owned U.S. Patents and U.S. Patent Applications

This application is a continuation-in-part of commonly owned U.S. Patent Application Serial No. 07/690,134, filed April 23, 1991, in the names of Christopher M. Looby et al. and entitled "Polymer Matrix Composite bodies and Methods For Making The Same."

Summary of the Invention

In accordance with the present invention, there is disclosed a plurality of materials and methods used to make self-supporting polymer matrix composite bodies. It has been unexpectedly discovered that when particular selection criteria for filler materials are combined with particular selection criteria for polymer materials, in combination with the processing methods of the invention, self-supporting polymer matrix composite bodies having very desirable properties, including desirable wear properties, can be produced.

Specifically, by focusing on the synergism between selected filler and polymer materials, desirable processing of self-supporting polymer matrix composite bodies is achieved, as well as resultant desirable wear resistant self-supporting polymer matrix composite bodies.

Filler materials useful in the present invention include wear resistant ceramic filler materials and wear resistant metallic filler materials.

An important aspect of the invention is the creation of a dilatant polymer/filler material mixture which assists in the shaping of the mixture into any desired shape. Specifically, by selecting particular combinations of filler materials and polymers, the mixture of materials can be caused to flow, by relatively mild vibrations, into even complex-shaped molds.

Once the dilatant mixture has assumed the shape of a mold, the polymer matrix is permitted to cure, thus forming a relatively rigid self-supporting polymer matrix composite body which can thereafter be removed from the mold.

Detailed Description of the Invention and Preferred Embodiments

In accordance with the present invention, there is disclosed a plurality of materials for use in a number of methods for producing self-supporting polymer matrix composite bodies. Specifically, various filler materials when used in combination with various polymers can result in desirable wear resistant self-supporting polymer matrix composite bodies.

In a first preferred embodiment of the invention, an appropriate filler material is chosen. The filler material is selected based on a number of different criteria including: composition; wear resistance of

- 5 -

the filler; the ability to obtain particle size distributions which permit packing of the filler within the polymer to occur; the shape of individual filler particles; the ability of the filler to be bonded to the polymer matrix; and the synergism between the filler and the polymer material both during processing and in the finished product. Further, the choice of an appropriate polymer material to function as a matrix for the polymer matrix composite is also dependent upon a number of different criteria. For example, the polymer should be capable of providing lubricity to the filler material thereby permitting the filler material particles to be wet by the polymer and to flow by each other relatively easily during the shaping of the mixture of polymer and filler under vibration; the polymer should have a low enough viscosity to permit mixing of the polymer and filler together and which viscosity and rheological behavior also permits the flow of the mixture of polymer and filler material under the process conditions of the invention; the polymer should not set up or harden too fast (e.g., have a long enough "pot life") so as to permit at least a partial packing of the filler material to occur and to permit a deairing or release of any trapped gases within the polymer matrix during processing; the polymer should have a relatively low shrinkage associated with it during curing; the polymer should be capable of being worked and cured at room temperatures or relatively low elevated temperatures; and it is preferable for the polymer per se to be wear and tear resistant.

Filler materials useful in the present invention include ceramic filler materials such as carbides (e.g., silicon carbide particulate, tungsten carbide particulate) oxides (e.g., alumina particulate), nitrides (e.g., aluminum nitride particulate), borides (e.g., titanium diboride), etc., with carbides being particularly preferred. Furthermore, under the processing conditions of the present invention, it is not a requirement for the ceramic filler materials to be pre-treated or coated to obtain a self-supporting polymer matrix composite body having desirable properties. Moreover, wear resistant metallic particles are also acceptable for use in the present invention.

It has been discovered that coarse grit silicon carbide particulate is a particularly desirable filler material. Most silicon carbide particulate is relatively inexpensive, readily available, wear resistant and has been found to bond to a number of desirable polymer materials used in the present invention without the need for pretreating or coating the

- 6 -

silicon carbide in any particular manner. A particularly attractive
filler is a coarse grit mixture of silicon carbide particulate. It is
believed that the large jagged surface area of coarse grit silicon carbide
serves to provide a better bond between the silicon carbide and the
5 polymer. It has been found that very desirable wear resistant properties
can be obtained by forming a mixture of about 10 parts per weight 14 grit
and 4 parts per weight 54 grit silicon carbide particulate within an
appropriate amount of a suitable polymer matrix. The above-mentioned
10 weight ratio provides for efficient packing yet still allows for bonding
between the silicon carbide and polymer to occur. Moreover, aggregate
blends of particulate having an average particle size of about 700-8000
microns present in an amount of about 50-100% by weight, when mixed with
particles having an average particle size of about 150-700 microns and
present in an amount of about 0-50% by weight, also produce desirable
15 packing and thus desirable wear results.

It is important for a proper combination of filler material mixture
and polymer to be chosen so as to provide for the synergistic effects
obtainable by utilizing the techniques of the present invention. For
example, if a particular filler material is desired to be included as a
20 reinforcement in a particular polymer, the mixture of filler material and
polymer should result in all of the benefits discussed above. Moreover,
the particular combination of filler material and polymer matrix should
result in the mixture being dilatant during shaping thereof. In this
context, dilatant is intended to mean that the mixture of polymer and
25 filler, before the polymer has cured, shows some shear thickening during
mixing, but has good flow characteristics under appropriate mild
vibrations. Accordingly, once the mixture of polymer and filler is
positioned within a particular mold by any suitable technique, gentle
vibrations of the mold cause the mixture to flow into even the most
30 complex details of the mold. Moreover, typically, the filler densely
packs within the polymer matrix, while remaining substantially
homogeneously distributed throughout the polymer matrix.

It has been discovered that a particularly useful polymer matrix
material is a wear resistant polymer having a viscosity of about 100-400
35 centipoise and even more preferably, about 150-250 centipoise. Such a
polymer, when mixed with a silicon carbide particulate, is capable of
providing lubricity to the mixture of polymer and silicon carbide, thus

causing the silicon carbide particulate to be thoroughly wet by the polymer and to flow by each other relatively easily. Moreover, it has been found that certain polymer materials having a viscosity of about 200 centipoise do not inhibit the mixing of the polymer and the filler material, but when thoroughly mixed result in a material with a consistency comparable to that of thick concrete. However, when this mixture is placed into a vibrating mold, the polymer and filler material will flow and conform to the interior dimensions of the mold and will permit an efficient, substantially homogeneous packing of the filler material within the polymer to occur. Additionally, it has been found that a low viscosity polymer facilitates deairing or release of trapped pores from within the polymer matrix. Numerous polymer materials are available that can provide the above-mentioned properties and, furthermore, can be processed at about room temperature.

It has been found that a proper ratio of filler material to polymer is an important aspect of the present invention. A particularly preferred ratio of about 70-80 percent by weight silicon carbide filler material to about 20-30 percent by weight polymer has shown very desirable properties. Moreover, depending on the relative densities of the filler material and polymer, weight ratios may differ. However, as discussed above, it is important for the mixture of filler material and polymer to be dilatant; thus, for example, appropriate volume percents of filler in the polymer matrix composite body range from about 50 to about 70 volume percent. In a preferred embodiment, when about 80 percent by weight silicon carbide particulate of the above-mentioned ratio (i.e., about 10 parts by weight 14 grit to about 4 parts by weight 54 grit) is mixed with about 20 percent by weight polymer material, the result is the mixture being dilatant, as discussed above. After thoroughly mixing the silicon carbide particulate and polymer material by any appropriate mechanical means, the resultant dilatant mixture is placed into a mold.

The mold can be formed into any shape and can be made of any material which does not adversely affect the processing or resultant properties of the polymer matrix composite. A particularly suitable mold material is silicone rubber. Specifically, silicone rubber molds do not adversely interact with any of the materials in the polymer matrix composite and can be shaped into virtually any shape. Moreover, silicone

rubber molds provide the flexibility to easily remove thereafter formed polymer matrix composites after the polymer has cured.

It has been further discovered that in most cases the amount of polymer provided for matrix should be as little as possible (e.g., just enough polymer to provide for sufficient bonding between the matrix and the filler material). When a small amount of polymer is provided relative to the filler, the amount of filler material present which is capable of enhancing the wear of the composite is maximized, thus potentially enhancing the wear properties of the composite. Moreover, polymers tend to be more expensive than most of the filler materials for use in the present invention, and thus it is probable that as the volume percent of filler increases, the cost of the composite body decreases, relative to a polymer which does not contain any filler.

It has been found that the frequency and amplitude of vibration experienced by the mixture contained within the mold is an important aspect of the present invention. If the vibration is too gentle, the mixture will not flow and conform to the interior dimensions of the mold, and if the vibration is too vigorous, the filler material will not pack properly and air bubbles will not be removed from the mixture.

It is preferred that the bond between the filler material and the polymer be stronger than the polymer itself, thereby minimizing the loss of filler material during wear applications. Such a bond can be a combination of both chemical and mechanical factors. Specifically, the chemistry of a surface of a filler material may enhance a chemical bond between the filler and a polymer matrix. In addition, the surface configuration of the filler may enhance a physical bond between the filler and the polymer. For example, with regard to a physical bond, it has been discovered that the more irregularly shaped the filler particle, the better the physical bond between the matrix and the filler. Moreover, the shape of the filler particle should be selected such that, when in combination with the polymer under the processing condition of the invention, only a small amount of settling of the filler relative to the matrix will occur. This small amount of settling, which typically occurs during the vibration steps of the present invention, will result in a substantially homogeneous self-supporting polymer matrix composite body.

As discussed above, the frequency and amplitude of vibration of the mold containing the mixture of polymer and filler is selected so as to

- 9 -

cause the mixture of polymer and filler to flow and to conform to the shape of the mold. In a preferred embodiment of the invention, the amount of settling of filler material relative to polymer matrix is minimized by providing only that amount of polymer which is necessary to wet the 5 surface of the filler material and bond, when hardened, the filler material in the polymer matrix. Once the composite mixture has assumed the shape of the mold, it is preferable that the mixture begin to harden by curing the polymer. However, as discussed above, the curing of the 10 polymer should not occur too rapidly such that the mixture is not given sufficient time to flow into the shaped mold.

Once the polymer has cured, the polymer can be removed from the mold and the self-supporting polymer matrix composite should then conform to the shape of the mold.

By following the above-mentioned processing steps, it has been found 15 that it is possible to produce a self-supporting silicon carbide reinforced polymer matrix composite material having a density of about 2.28 g/cc which is the equivalent of about 56 volume percent filler or about 79 weight percent filler. The silicon carbide particulate is thoroughly packed in a homogeneous manner throughout the polymer matrix.

Furthermore, it has been discovered that by using the above-mentioned ratios of filler material and polymer, as well as a polymer having a relatively low viscosity, there is surprisingly very little segregating of the filler material when vibration is applied to the mold. Due to this unique feature of the invention, there are few, if any, shape 25 or size limitations for self-supporting polymer matrix composites formed according to the invention. Specifically, the invention is not limited to the production of, for example, plates where only one side of the plate has a high filler concentration due to the settling of filler material in the polymer matrix. If such settling occurs, one side of a plate has very 30 different wear properties from the other side of the plate. Thus, due to the lack of filler segregation in the present invention, any number of complex-shaped parts may be fabricated, such shapes being limited only by the ability to produce complex mold shapes. Since the filler is substantially uniformly dispersed throughout the part, wear properties of 35 the part are substantially consistent throughout. One skilled in the art can readily appreciate the numerous wear parts that can thus be produced utilizing the methods of the present invention.

- 10 -

However, it is possible to vary the ratio of polymer to filler so that at least some segregation of filler would occur. In certain cases it may be desirable to produce nonhomogeneous self-supporting polymer matrix composite bodies.

5 Various demonstrations of the present invention are included in the Examples immediately following. However, these Examples should be considered as being illustrative and should not be construed as limiting the scope of the invention as defined in the appended claims.

10 Example 1

This Example demonstrates a method for producing a self-supporting silicon carbide reinforced polymer matrix composite material. Specifically, about 3500 grams of 14 grit, 39 CRYSTOLON® green silicon carbide particulate (Norton Company, Worcester, MA), and about 1500 grams of 54 grit, 39 CRYSTOLON® green silicon carbide particulate were poured into a two quart plastic storage container (Fischer Scientific, Pittsburgh, PA). The silicon carbide particulate mixture was thoroughly mixed utilizing a plastic stirring rod. A temperature of about 200°F was established within an ISOTEMP® 500 series drying oven (Fischer Scientific, Pittsburgh, PA) and the plastic container and its contents were placed within the drying oven.

20 About 1400 grams of Uniroyal B601 VIBRATHANE® prepolymer (Uniroyal Chemical Company, Inc., Middlebury, CT) was poured into a 1 gallon plastic storage container (Fischer Scientific, Pittsburgh, PA) and the container and its contents were placed within the ISOTEMP® 500 series oven.

25 About 271.5 grams of 4,4'-methylene-bis-(ortho-chloroaniline), (commonly referred to as MOCA) curative pellets were poured into a 400 ml tri-cornered plastic beaker (Fischer Scientific, Pittsburgh, PA). A temperature of about 212°F was established within a Model 850 C 100 drying oven (Gruenberg Oven Company, Inc., Williamsport, PA) and the tri-cornered beaker and its contents were placed into the oven.

30 After about 1/2 hour, the one-gallon plastic storage container containing the prepolymer was removed from the ISOTEMP® 500 series drying oven and placed into a Super Vac-Mac vacuum bell jar (Rey Industries, Inc.). The vacuum bell jar was evacuated to about 28 mm mercury. After about 5 minutes, ambient pressure was reestablished within the vacuum bell jar and the plastic container and prepolymer were removed from the vacuum

- 11 -

bell jar and returned to the ISOTEMP® 500 series drying oven for an additional 1/2 hour.

After remaining in the Model 850 C 100 drying oven for about 1 hour, the plastic tri-cornered beaker containing the MOCA curative pellets was removed from the oven, and it was noted that substantially all of the pellets had melted. The plastic tri-cornered beaker and MOCA curative were quickly placed under a fume hood. The one-gallon plastic storage container and the prepolymer were then removed from the ISOTEMP® 500 series drying oven and the now liquid MOCA curative was poured into the one-gallon plastic storage container containing the prepolymer. The prepolymer and MOCA were thoroughly mixed with a plastic spoon. After mixing the MOCA and prepolymer, the one-gallon plastic storage container and its contents were quickly placed within the vacuum bell jar. The vacuum bell jar was evacuated to about 28 mm mercury. This level of vacuum was held for about 30 seconds, and then ambient pressure was reestablished within the vacuum bell jar. The one-gallon plastic storage container and its contents were quickly removed from the vacuum bell jar. The two-quart plastic container containing the silicon carbide particulate mixture was removed from the ISOTEMP® 500 series drying oven and poured into the one-gallon plastic storage container containing the prepolymer/MOCA mixture. The prepolymer/MOCA/silicon carbide particulate was mixed with a plastic spoon such that each silicon carbide particle was wet by the prepolymer/MOCA mixture. It was noted that the mix had the consistency comparable to that of thick concrete.

A Grade GI-1000 silicone rubber mold (Plastic Tooling Supply Company, Exton, PA) having internal dimensions of about 12 inches x 12 inches x 1.5 inches deep was placed on a Model VP-51-D1 vibrating table (FMC, West Reading, PA). As shown in Figure 1, the prepolymer/MOCA/silicon carbide particulate mixture 1 was scooped out of the one-gallon plastic storage container and into the center of the rubber mold 2. The vibrating table was turned on and set at a low vibration speed. The rubber mold was subjected to gentle vibration (approximately 4 on the vibrating table control knob) causing the prepolymer/MOCA/silicon carbide particulate mixture, as shown in Figure 2 and 3, to conform to the inner dimensions of the mold and causing entrapped air to be removed from the mixture. As more prepolymer/MOCA/silicon carbide particulate mixture was scooped into the mold, the vibration was increased so that the mixture

- 12 -

continued to conform to the inner dimensions of the mold. After about 5 minutes of vibration, the vibrating table was turned off and the rubber mold and its contents were removed from the vibrating table and placed within the Model 850 C 100 drying oven. The temperature within the drying oven was maintained at about 212°F for about 6 hours. After about 6 hours, the mold and its contents were removed from the oven and allowed to cool to room temperature. After cooling, the mold was inverted and the resultant 12 inch x 12 inch x 1 inch self-supporting polymer matrix composite material was removed from the mold.

10

Example 2

This Example further demonstrates a method for producing a self-supporting silicon carbide reinforced polymer matrix composite material. Specifically, about 850 grams of 14 grit 39 CRYSTOLON® green silicon carbide particulate (Norton Company, Worcester, MA) and about 350 grams of 54 grit 39 CRYSTOLON® green silicon carbide particulate were poured into a two-quart plastic storage container (Fischer Scientific, Pittsburgh, PA). The silicon carbide particulate mixture was thoroughly mixed utilizing a plastic stirring rod.

20

About 250 grams of RP6413 prepolymer (Ciba-Geigy, Wilmington, DE) was poured into a one-gallon plastic storage container (Fischer Scientific, Pittsburgh, PA). About 150 grams of RP6413 hardener (Ciba-Geigy, Wilmington, DE) was poured into a 400 ml tri-cornered plastic beaker (Fischer Scientific, Pittsburgh, PA).

25

The one-gallon plastic storage container and the prepolymer were placed into a Super Vac-Mac vacuum bell jar (Rey Industries, Inc.). The vacuum bell jar was evacuated to about 28 mm mercury. After about 5 minutes, ambient pressure was reestablished within the vacuum bell jar and the plastic container and prepolymer were removed from the vacuum bell jar. The RP6413 hardener was poured from the tri-corner beaker into the one-gallon plastic storage container containing the prepolymer and the prepolymer and hardener were mixed utilizing a plastic spoon. The one gallon plastic storage container and its contents were quickly placed within the vacuum bell jar and the vacuum bell jar was evacuated to about 28 mm mercury. After about 30 seconds, ambient pressure was reestablished within the vacuum bell jar, and the one-gallon plastic storage container and its contents were removed and placed under a fume hood.

- 13 -

The silicon carbide particulate mixture was quickly poured into the one-gallon plastic storage container containing the prepolymer/hardener mixture. The prepolymer/hardener/silicon carbide particulate was mixed with a plastic spoon such that each silicon carbide particle was wet by the prepolymer/hardener mixture. It was noted that the mix had the consistency comparable to that of thick concrete.

A Grade GI-1000 silicone rubber mold (Plastic Tooling Supply Company, Exton, PA) having internal dimensions of about 7 inches x 5 inches by 1.5 inches deep was placed on a Model VP-51-D1 vibrating table (FMC, West Reading, PA). The prepolymer/hardener/silicon carbide particulate mixture was scooped out of the one-gallon plastic storage container and into the center of the rubber mold. The vibrating table was turned on and set at a low vibration speed. The rubber mold was subjected to gentle vibration (approximately 4 on the vibrating table control knob) causing the prepolymer/hardener/silicon carbide particulate mixture to conform to the inner dimensions of the mold and causing entrapped air to be removed from the mixture. As more prepolymer/hardener/silicon carbide particulate mixture was scooped into the mold, the vibration was increased so that the mixture continued to conform to the inner dimensions of the mold. After about 5 minutes of vibration, the vibrating table was turned off and the rubber mold and its contents were removed from the vibrating table and placed within a Model 850 C 100 drying oven (Gruenberg Oven Company, Inc., Williamsport, PA). A temperature of about 180°F was established within the drying oven. After about 16 hours, the mold and its contents were removed from the oven and allowed to cool to room temperature. After cooling, the mold was inverted and the resultant about 7 inch x 5 inch x 1 inch self-supporting polymer matrix composite material was removed from the mold.

- 14 -

Claims

1. A method for making a self-supporting polymer matrix composite body comprising:
 - selecting a filler material;
 - selecting a polymer material;
 - mixing said polymer material and filler material together in amounts which result in the mixture becoming dilatant;
 - placing the dilatant mixture into a mold;
 - vibrating the mold at a frequency and amplitude which cause the dilatant mixture to flow and assume the shape of the mold; and
 - curing the polymer to form a self-supporting polymer matrix composite body.
2. The method of claim 1, wherein said filler material comprises at least one of a ceramic filler material and a metallic filler material.
3. The method of claim 2, wherein said ceramic filler material comprises at least one material selected from the group consisting of carbides, oxides, nitrides and borides.
4. The method of claim 3, wherein said filler material comprises a silicon carbide or tungsten carbide filler material.
5. The method of claim 4, wherein said filler material comprises silicon carbide and is provided in an amount of about 70-80 weight percent and said polymer material is provided in an amount of about 20-30 weight percent.
6. The method of claim 4, wherein said ceramic filler material comprises a mixture of about 50-100 percent by weight of about 700-8000 micron average particle size and about 0-50 percent by weight of about 150 micron to about 700 micron average particle size.
7. The method of claim 5, wherein said filler material comprises a mixture of about 10 parts per weight 14 grit silicon carbide particulate and about 4 parts per weight 54 grit silicon carbide particulate.

- 15 -

8. The method of claim 1, wherein said polymer comprises a wear resistant polymer.

5 9. The method of claim 1, wherein said polymer has a viscosity of from about 100 to about 400 centipoise during mixing of said polymer material with said filler material.

10 10. The method of claim 8, wherein said wear resistant polymer comprises at least one polymer selected from the group consisting of polyester and polyether urethanes.

15 11. The method of claim 1, wherein said filler material is provided in an amount of about 50-70% by volume in the formed self-supporting polymer matrix composite body.

12. A wear resistant self-supporting polymer matrix composite body comprising:

about 70-80 percent by weight filler; and;

20 about 20-30 percent by weight wear resistant polymer, wherein said polymer comprises a matrix which embeds said filler and wherein said filler is substantially homogeneously distributed throughout said polymer.

25 13. The self-supporting polymer matrix composite body of claim 12, wherein said filler comprises at least one material selected from the group consisting of wear resistant ceramic particulate and wear resistant metallic particulate.

30 14. The self-supporting polymer matrix composite body of claim 13, wherein said particulate comprises at least one of silicon carbide and tungsten carbide.

35 15. The self-supporting polymer matrix composite body of claim 14, wherein said silicon carbide filler is present as a mixture comprising an amount of about 50-100 percent by weight of an average particle size of about 700-8000 microns and about 0-50 percent by weight of an average particle size of about 150- 700 microns.

- 16 -

16. A self-supporting polymer matrix composite body comprising:
about 50-70 percent by volume filler; and
about 30-50 percent by volume polymer, wherein said polymer
comprises a matrix which embeds said filler and wherein said filler is
substantially homogeneously distributed throughout said polymer.

5

1/1

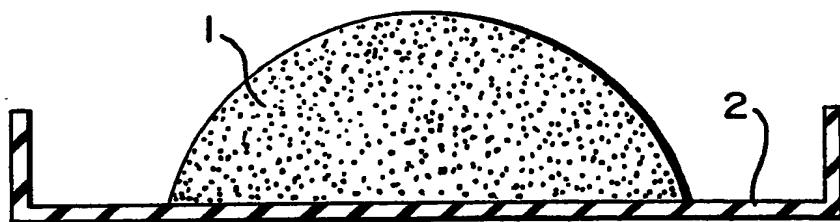


Fig - 1

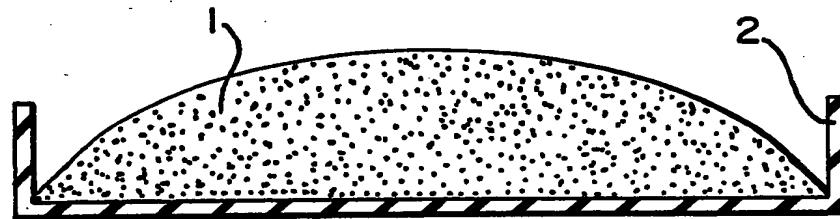


Fig - 2

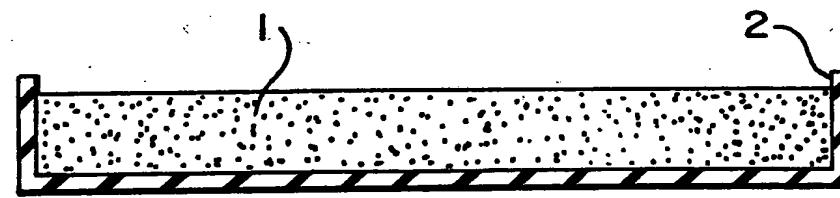


Fig - 3

CIRSTITIITE SHEET

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)¹

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.C1. 5 B29C67/24

II. FIELDS SEARCHED

Minimum Documentation Searched²

Classification System	Classification Symbols
Int.C1. 5	B29C

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched³III. DOCUMENTS CONSIDERED TO BE RELEVANT⁴

Category ⁵	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	FR,A,2 242 344 (TOUATI) 28 March 1975 see the whole document ---	1-16
A	US,A,2 751 775 (SERGOVIC) 26 June 1956 cited in the application ---	1-16
X	GB,A,1 127 460 (KOPPERS COMPANY) 18 September 1968 see page 1, line 61 - page 2, line 3 see page 2, line 71 - line 107 see page 3, line 33 - line 60 see page 4, line 22 - line 34 ---	12-16
A	DE,A,2 408 503 (HOEDT) 4 September 1975 see page 11, line 8 - line 15 see page 12, paragraph 4 see claim 1 ---	1-12
A	DE,A,2 408 503 (HOEDT) 4 September 1975 see page 11, line 8 - line 15 see page 12, paragraph 4 see claim 1 ---	1-16
		-/-

⁶ Special categories of cited documents :¹⁰

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

- "Z" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

04 SEPTEMBER 1992

Date of Mailing of this International Search Report

15.09.92

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

SCHÖLVINCK T. S.

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category ^a	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	US,A,3 585 100 (GREENLEES) 15 June 1971 cited in the application see column 3, line 6 - line 14. -----	1,12

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. US 9203293
SA 60530**

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 04/09/92

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
FR-A-2242344	28-03-75	None	
US-A-2751775		None	
GB-A-1127460		None	
DE-A-2408503	04-09-75	None	
US-A-3585100	15-06-71	None	